

Supplementary information

Light-Enhanced Microcontact Printing of 1-Alkynes onto Hydrogen-Terminated Silicon

Jurjen ter Maat, Menglong Yang, Luc Scheres, Stefan Kuypers and Han Zuilhof*

Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands, and JEOL (Europe) BV, Leuvensesteenweg 542, B-1930 Zaventem, Belgium.

1. XPS wide area spectrum

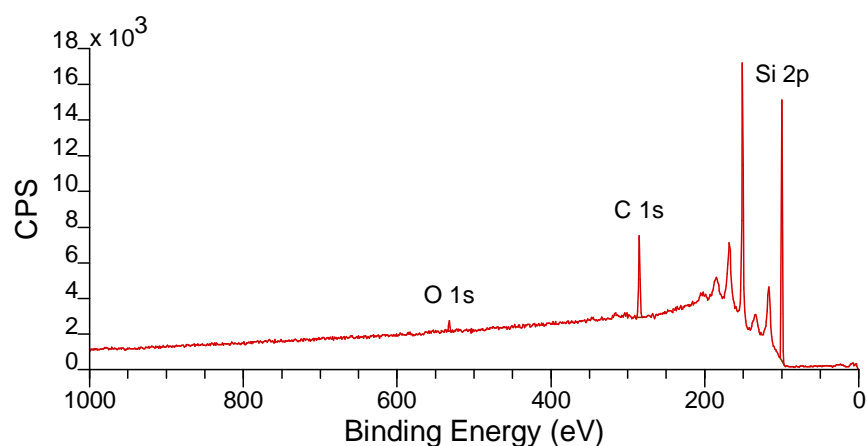


Figure S1. XPS wide area spectrum of a sample that was obtained after LE-mCP (3 h, 658 nm) with 1-octadecyne using a flat stamp

2. Influence of illumination wavelength

It is known that light in the UV and visible range can induce monolayer formation on Si.¹ Even though the mechanism is not fully understood, it is thought that excitation of Si electrons to the conduction band plays a role in the mechanism.² As the bandgap of Si is only 1.1 eV, this can be done with any visible light wavelength. Indeed, it was observed that after illumination with either 447 or 658 nm patterns were well transferred and the feature height was not significantly different, ~ 1.4 nm. Illuminating with 254 nm, however, only resulted in a faint pattern in the phase image. These results cannot be sufficiently explained by the decreased transmission of UV light compared to visible light, since the experiment without illumination did show a pattern in the AFM height image. Instead, it may be the UV absorption of the stamp that induces a side reaction. This was supported by AFM imaging of the printed samples prior to etching, which showed the formation of ring-shaped structures of several nanometers in height (Figure S2). These structures could withstand ultrasonication and Soxhlet extraction, but could be removed by etching with NH_4F solution. Therefore, it is likely that they are chemisorbed, and contain siloxane fragments originating from the stamp, such as the alkene-terminated PDMS fragments that function as crosslinking agents in commercial PDMS kits.³ Presumably, the side reaction in the stamp and/or the formation of ring-shaped structures competes

effectively with monolayer formation, since no monolayer formation is observed at all. For the formation of similar ring-shaped structures upon long-contact printing, it has been proposed that this originates from migration of PDMS residues from the vertical walls of the stamp, resulting in accumulation at the stamp/surface/air interface.⁴ In addition, alkenes are photoreactive under UV illumination, and thus may initiate side reactions, at the surface, but also within the stamp, resulting in decreased diffusion of alkyne to the surface. To prevent these side reactions, 658 nm light was selected for further experiments.

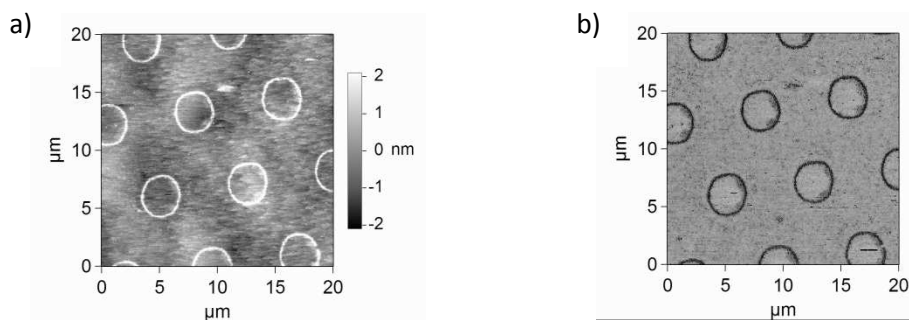


Figure S2. AFM images of a patterned Si(111) sample obtained by LE- μ CP (254 nm, 3 h) with 1-octadecyne: a) height image before etching b) corresponding phase image

3. Influence of inking parameters

As high local concentrations are required,⁵ it is likely that the amount of ink available at the stamp-surface interface can become a limiting factor during the process. In addition, our reference experiments indicated the transport of ink from the bulk to the surface of the stamp. Thus, saturating the stamp with ink might overcome the limitations in monolayer formation. Therefore, two inking parameters were varied: the inking concentrations and the stamp immersion time.

In regular experiments, stamps were inked in a 100 mM 1-octadecyne solution. Inking the stamp in a 10 mM solution resulted in decreasing feature heights: the pattern was barely visible by AFM. This shows that at these low concentrations, the amount of available ink is indeed limiting the monolayer formation. However, increasing the inking concentration to 500 mM did not result in higher features. In addition, practical difficulties were encountered due to saturation of the solution. Upon drying, this can result in a non-uniform ink film or crystallization on the stamp surface. Therefore, increasing the inking concentration above 100 mM is not recommended.

Alternatively, the stamp immersion time could be varied. Whereas prolongation of the immersion time from 2 to 10 min in a solution of 10 mM alkyne resulted in slight improvement of the feature height, this was not the case for the 100 mM solution. This shows that the saturation level of ink in the stamp did not change significantly in the latter case. Printing with a stamp that was saturated with ink by overnight immersion could not be performed due to the lack of interaction between stamp and surface, which prevented conformal contact. Thus, we were unable to further improve the feature height by changing the inking parameters, indicating that the amount of available ink is not the limiting step in LE- μ CP.

One other possible limitation may be the undesired reaction of ethanol with the surface. Ethanol was selected as a solvent because it hardly swells PDMS and it can dissolve apolar compounds such as alkynes. However, it is also known to react with Si-H, which could lead to the formation of a mixed monolayer in the presence of 1-octadecyne. This monolayer would have a disordered character due to the short chain length of surface bound ethanol, and thus would have a limited thickness. Even though no direct evidence of ethoxysilyl formation was found (e.g. Si-O peaks in the XPS Si_{2p} spectrum),

ethanol reaction cannot be fully excluded. Thus, one way of improving the monolayer quality in LE- μ CP may be the use of a non-reactive inking solvent. Ideally, this solvent should not swell PDMS and dissolve alkynes well. Alternatively, the solvent could be excluded at all. However, inking in a neat liquid is likely to result in the loss of resolution due to filling of the voids. And similar to the stamps that were saturated from ethanolic alkyne solution, these stamps will not have much interaction with the Si-H surface, preventing conformal contact. These problems may be avoided by using a different inking strategy, as has been introduced by Balmer et al.⁶ Here, an ink reservoir is placed on the backside of the stamp, which induces ink diffusion through the stamp towards the molded side. Possible side effects caused by solvents are excluded simply because this strategy does not require any. Further investigation is necessary to combine this inking strategy with backside illumination.

4. Artificial height differences in AFM imaging of backfilled samples

Whereas regular AC-AFM measurements of the C18/TFEE and TFEE/C18 samples hardly showed any topographical features, imaging in the non-contact regime (phase signal $> 90^\circ$) with a weak cantilever resulted in clear contrast in the height image (Figure 4 top). This height artifact (> 2 nm of the C18 area relative to TFEE area) is caused by different interaction forces between the AFM tip and the monolayer surfaces. The fluoroalkyl end-capped TFEE ester areas possess a lower surface energy than the alkyl-terminated C18 areas, and as a result the AFM tip approaches the former more closely than the latter under the same feedback settings, thus yielding artificial height differences. As the force differences are relatively small, a weak cantilever is required to observe this effect.

5. Experimental section

Materials. De-ionized water (with a resistivity of 18.3 M Ω cm) was used for sample cleaning. Acetone (semiconductor grade, Riedel de Haen), cyclohexane (anhydrous, Sigma-Aldrich), 40% NH₄F solution (semiconductor grade, Honeywell), sulfuric acid (95-97 %, Sigma-Aldrich), hydrogen peroxide (30 %, Sigma-Aldrich) and PDMS precursors (Sylgard 184, Dow Corning) were used as received. EtOH and CH₂Cl₂ were distilled prior to use. 1-Octadecyne was synthesized from 1-bromohexadecane and lithium acetylide ethylene diamine complex as described elsewhere,⁷ and purified by column chromatography, recrystallization and vacuum distillation. 2,2,2-Trifluoroethyl undec-10-ynoate was synthesized from 2,2,2-trifluoroethanol and 10-undecynoic acid as described elsewhere,⁸ and purified by flash column chromatography. Silicon wafers were (111)-oriented single-side and double polished, 475 - 550 μ m thick, n-type, P-doped samples, with a resistivity 1.0-5.0 Ω cm (Siltronix, France).

Stamp fabrication. Stamps were made by casting a PDMS prepolymer mixture onto a patterned silicon master. The stamps were cast from a silicon master with a hexagonal pattern of 4 μ m wide wells, with a period of 8 μ m. After degassing the mixture for 60 min under vacuum, the polymer-covered master was annealed at 60 $^\circ$ C for > 48 h. The polymer was removed from the master and subsequently cut into stamps of 1 \times 1 cm. These were extracted with ethanol by overnight Soxhlet extraction, dried at 50 $^\circ$ C under vacuum, and stored. Prior to use, stamps were cleaned by 5 min ultrasonication in ethanol.

Light-enhanced microcontact printing. A piece of n-type Si(111) was cleaned by wiping with an acetone-soaked piece of cotton, followed by ultrasonication for 5 min in acetone, and then in water. The sample was subsequently immersed into a freshly prepared piranha solution (7 parts H₂SO₄ mixed

with three parts 30 % H₂O₂. *Caution: Piranha is a very strong oxidizer and can react explosively with organic compounds*). After 15 min, the sample was rinsed copiously with degassed, de-ionized water and was then etched for 15 min in an argon-saturated aqueous solution of 40 % NH₄F. Afterwards, the sample was rinsed with water, shortly ultrasonicated with water, and dried in a stream of argon. It was mounted on a magnetic base and transferred into a glovebox with O₂ and H₂O levels typically below 1 ppm.

Simultaneously to sample cleaning and etching, a stamp was immersed in a solution of alkyne in ethanol (typically 2 min in 100 mM 1-octadecyne), blown dry with argon and then further dried under vacuum for 30 min. It was transferred to the glovebox, where it was contacted to the etched silicon sample. A thin metal frame was carefully placed on top, which ensures contact throughout illumination, because of the attractive force of the magnetic base. The sample was covered with a long pass filter, and then illuminated with a phosphor-coated, low-pressure mercury lamp (Jelight, Irvine, CA). In a typical experiment, illumination was performed for 3 h with a lamp designed to emit at 658 nm, in combination with a 395 nm long pass filter. After illumination, the sample was taken from the glovebox and cleaned by ultrasonication in ethanol, and in dichloromethane (5 min each). It was further cleaned by Soxhlet extraction in cyclohexane (> 30 min), shortly ultrasonicated with ethanol and water, and etched in an argon-saturated 40 % NH₄F solution for 1 min. Finally, the sample was rinsed and ultrasonicated with water, dried with argon and taken to the AFM or further modified in a backfilling step.

Monolayer backfilling. Backfilling of patterned samples was performed using the modification procedure reported by Scheres et al.⁹ Briefly, the etched sample was transferred to a three-neck flask charged with neat, deoxygenated alkyne under argon overflow. The flask was equipped with a capillary argon inlet and with a condenser connected to a Schlenk line. The flask was closed, its pressure was reduced to approximately 10 mbar (the inert atmosphere being maintained by argon flowing through the capillary), and it was immersed in an oil bath at 80 °C. After 16 h, the flask was backfilled with argon until atmospheric pressure was attained, and the sample was taken out. After rinsing excessively with ethanol and CH₂Cl₂ and sonication in CH₂Cl₂ for 5 min to remove physisorbed molecules, the sample was blown dry with a stream of dry nitrogen.

Atomic Force Microscopy. AFM images were obtained in tapping mode (AC-AFM) with an MFP3D instrument (Asylum Research, Santa Barbara, CA) using NSC35 3-lever probes (MikroMasch, Estonia). Usually, the A-type cantilever (210 kHz, 7.5 N/m) was used, except for imaging the backfilled samples, when the C-type cantilever (150 kHz, 4.5 N/m) was used. Images were flattened with the MFP3D software.

Scanning Electron Microscopy. Scanning electron micrographs were obtained with a JEOL JCM-5000 NeoScope using the secondary electron detector. The electron acceleration voltage was 5 kV. For the backfilled samples, the image contrast was enhanced using ImageJ 1.43u.

X-ray Photoelectron Spectroscopy. XPS analysis was performed with a JPS-9200 Photoelectron Spectrometer (JEOL, Japan). High-resolution spectra were obtained under UHV conditions using monochromatic Al K α X-ray radiation at 12 kV and 25 mA, using an analyzer pass energy of 10 eV. The X-ray incidence angle and the electron acceptance angle were 80° and 10° with respect to the surface normal, respectively. Spectra were corrected with a linear background subtraction before quantification and any peak deconvolution.

Ellipsometry. Ellipsometric measurements were performed with a Sentech Instruments (Type SE-400) ellipsometer, operating at 632.8 nm (He-Ne-laser) and an angle of incidence of 70°. The optical

constants of the substrate were determined with a piece of freshly etched n-Si(111) ($n = 3.713$ and $k = 0.088$). The thickness of the monolayer was determined with a planar three-layer (ambient, monolayer, substrate) isotropic model with refractive index of 1.46 for the organic monolayer. The reported value is the average of 20 measurements taken at multiple locations on the sample.

Water contact angle measurements. Static contact angles were measured using a Krüss DSA-100 goniometer. Droplets of 3 μl were dispensed on the surface and contact angles were measured with a CCD camera using a tangential method. The reported value is the average of 5 droplets measured on different positions on the surface.

6. References

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